FENPROPATHRIN (185)

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EXPLANATION

Fenpropathrin, an insecticide/acaricide, was first evaluated by JMPR in 1993 as a new compound. At that time the Meeting allocated an ADI of 0-0.03 mg/kg and recommended 14 MRLs, later adopted by the Codex Alimentarius Commission in 1995 or 1997 as Codex MRLs. The residue definition is fenpropathrin (residue is fat soluble).

At the 38th Session of the CCPR in 2006, the Delegation of India requested the elaboration of an MRL for tea. Fenpropathrin was added to the agenda of the current Meeting for the evaluation its use on tea, pending availability of data. The Meeting received the current label in India, results of supervised residue trials, processing and plant metabolism studies and methods of analysis.

Plant metabolism

The 1993 JMPR reviewed plant metabolism studies on apple, beans, cotton and tomato and concluded that fenpropathrin itself was the primary component of the residues in the fruits of plants but degradation products constituted the greater part of the residues present in the leaves. In addition, the 1993 JMPR concluded that any uptake of residues from the soil is too slow for detectable residues to occur in succeeding crops, especially in view of the comparatively short persistence of the compound in soils.

The current Meeting received studies conducted to determine the metabolism of fenpropathrin in leaves.

Cabbage

The metabolism of radio-labelled fenpropathrin was investigated in cabbages grown and treated in a greenhouse (Mikami *et al.*, 1983; Report No. FM-30-0009). Fenpropathrin labelled at either the cyano group (referred to as ¹⁴CN), or the C1 position of the cyclopropyl ring (cyclopropyl-¹⁴C), or the benzylphenyl ring (benzyl-¹⁴C) was dissolved in methanol and evenly applied to the upper surface of two 3rd-4th leaves of cabbage seedlings at a rate of 22 µg per leaf. The cabbages were sampled immediately after application and at 3, 7, 14, 21, 28, 35 and 42 days after application.

The cabbage samples were separated into treated leaves and un-treated shoot portions. The treated leaves were rinsed twice with methanol and the radioactivity in the wash, leaves and untreated shoots determined. The leaves and the untreated shoots were separately homogenized and extracted with a solution of methanol:chloroform:distilled water (4:2:1). Metabolites in cabbages treated with ¹⁴C-fenpropathrin were identified by thin layer chromatography (TLC). Metabolites present on TLC from three labelled preparations were compared to distinguish products retaining the ester linkage from hydrolysis products. The extractable components in cabbages harvested 28 and 42 days after application are shown in Table 1.

Table 1. Extractable components in cabbage samples harvested 28 and 42 days after application. (Mikami *et al.*, 1983; Report No. FM-30-0009).

	% of the applied ¹⁴ C					
	Cyclopropyl-14C		¹⁴ CN		Benzyl-14C	
	28 days	42 days	28 days	42 days	28 days	42 days
Surface Wash:						
Fenpropathrin	0.6	0.3	1.0	0.6	1.7	0.4
Others	0.3	0.1	0.4	0.3	0.3	0.1
Surface Wash Total	0.9	0.4	1.4	0.9	2.0	0.5

			% of the ap	oplied ¹⁴ C		
	Cyclopr	opyl- ¹⁴ C	14	CN	Benz	yl- ¹⁴ C
	28 days	42 days	28 days	42 days	28 days	42 days
methanol:chloroform:distilled water (4:2:1) Extr	acts:					
Fenpropathrin	15.8	11.7	16.9	6.0	12.9	11.3
CONH ₂ -fenpropathrin	0.7	< 0.1	0.3	< 0.1	0.9	< 0.1
COOH-fenpropathrin	0.4	0.4	0.6	0.3	0.7	< 0.1
2'-OH-fenpropathrin	0.1	< 0.1	0.4	< 0.1	0.4	< 0.1
Fenpropathrin-CH ₂ OH	0.4	0.3	0.5	0.5	0.6	0.2
TMPA-lactone	0.1	< 0.1	-	-	-	-
TMPA-CH ₂ OH-lactone	0.8	0.9	-	-	-	-
COOH-fenpropathrin-conjugate	0.4	0.2	0.6	0.4	0.6	0.7
2'-OH-fenpropathrin-conjugate	0.2	0.1	0.1	0.1	0.1	0.2
4'-OH-fenpropathrin-conjugate	1.3	0.7	1.6	1.0	0.6	0.8
Fenpropathrin-CH ₂ OH-conjugate	3.5	4.0	3.4	4.3	4.2	4.0
2'-OH-fenpropathrin-CH ₂ OH-conjugate	4.8	4.5	4.6	4.5	5.9	6.2
4'-OH-fenpropathrin-CH ₂ OH-conjugate	4.0	4.3	4.0	4.5	3.9	0.2
2'-OH-fenpropathrin-(CH ₂ OH) ₂ -conjugate	20.3	22.0	18.6	20.7	19.4	21.6
4'-OH-fenpropathrin-(CH ₂ OH) ₂ -conjugate	20.3	22.0	16.0	20.7	17.4	21.0
TMPA-conjugate	0.9	0.8	-	-	-	-
TMPA-CH ₂ OH-conjugate	1.1	1.0	-	-	-	-
TMPA-COOH-conjugate	3.7	4.2	-	-	-	-
TMPA-CH ₂ OH-lactone-conjugate	11.3	11.1	-	-	-	-
Pbalc-conjugate	-	-	-	-	0.1	0.1
Pbacid-conjugate	-	-	-	-	0.8	1.1
2'-OH-Pbacid-conjugate	-	-	-	-	6.9	7.4
4'-OH-Pbacid-conjugate	-	-	-	-	4.5	4.6
Others	5.2	5.8	4.2	5.8	9.6	9.1
Extracts Total	71.0	67.7	51.8	43.6	68.2	67.3
Unextractable ¹⁴ C Total	2.6	5.1	6.7	11.3	4.0	7.5
Treated Leaves Total	74.5	73.2	59.9	55.8	74.2	75.3
Untreated Shoots	0.9	1.2	0.6	0.7	0.4	0.4
Overall Total	75.4	74.4	60.5	56.5	74.6	75.7

The study demonstrated that after foliar application of ¹⁴C-fenpropathrin to cabbages the radioactive carbon remaining on the surface of treated leaves decreased, as ¹⁴C in the leaves increased. Most of the recovered radioactivity was in the treated leaves and less than 1.2% of the applied radioactivity was found in the untreated shoots indicating that there is little translocation of fenpropathrin and its metabolites from the application site to other parts of the plant.

TLC showed that, in all cases, the predominant radioactive component in the surface washes was the parent compound. Fenpropathrin underwent ester cleavage, hydrolysis of the –CN group to the –CONH₂ and the –COOH groups, hydroxylation at either or both of the gem-dimethyl group with subsequent oxidation to carboxylic acid, and hydroxylation at the 2'- or 4'-position of the phenoxy group. Most of the resultant carboxylic acids and alcohols occurred as glycoside conjugates in plants.

Abscised leaves of apple, cabbage, kidney bean, mandarin orange, tomato and vine

Mikami *et al.*, (1983; Report No. FM-30-0009) also conducted a study on the fate of HCN and 2,2,3,3-tetramethylcyclopropanecarboxylic acid (TMPA) in abscised leaves of apple, cabbage, kidney bean, mandarin orange, tomato and vine. TMPA labelled at the C1 position of the cyclopropyl ring (¹⁴C-TMPA) was prepared. Two abscised leaves from each plant were placed in 100 mL distilled water containing ¹⁴C-TMPA at a concentration of 1.0 ppm. After cultivation for five days, the leaves were extracted with methanol:chloroform:water (4:2:1). In a separate experiment, abscised leaves of cabbage and bean plants were placed in a 100 ppm solution of ¹⁴C-TMPA in order to obtain large quantities of metabolites for characterization. The extracts were partitioned between ethyl ether and distilled water. After acidification the aqueous layer was partitioned with ethyl acetate. The extractable components in abscised leaves of various plants over a 5 day period are shown in Table 2.

Table 2. Extractable components in abscised leaves of various plants over a 5 day period. (Mikami *et al.*, 1983; Report No. FM-30-0009)

			% of the a	pplied ¹⁴ C		
	Apple	Bean	Cabbage	Orange	Tomato	Vine
Extracts:						
TMPA	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
TMPA-Gu	21.5	14.7	3.2	3.0	2.0	6.6
CH₂OH-TMPA-Gu	5.2	3.2	3.4	0.2	0.2	0.4
TMPA-CH₂OH-Gu	1.3	-	-	-	-	0.1
TMPA-Gu-Gu	5.4	2.8	-	-	12.8	0.7
TMPA-malonyl-Gu	0.7	56.2	70.5	3.1	4.3	0.1
CH ₂ OH-TMPA-malonyl-Gu	-	-	1.5	0.4	-	-
Others	1.5	3.0	0.2	0.5	1.1	0.2
Extracts Total	35.6	79.9	78.8	7.2	20.4	8.1
Unextractable ¹⁴ C Total	0.3	0.2	0.2	0.4	0.2	0.3
Abscised Leaves Total	35.9	80.1	79.0	7.6	20.6	8.4
Aqueous Solution:						
TMPA	57.1	24.5	13.2	63.8	76.1	83.0
Others	1.2	0.8	0.9	0.7	1.6	0.5
Aqueous Solution Total	58.3	25.3	14.1	64.5	77.7	83.5
Overall Total	94.2	105.4	93.1	72.1	98.3	91.9

TMPA was readily converted in plants to more polar products. In orange, cabbage and bean plants, the malonylglucoside was mainly formed. In tomato, the gentiobioside was predominant.

Further work was carried out using K¹⁴CN. Two abscised cabbage leaves were treated for four hours with distilled water containing K¹⁴CN and then transferred to K¹⁴CN-free distilled water. The treated leaves were extracted at specific intervals after dosing with K¹⁴CN, and the extracts were subject to TLC.

There was a gradual increase in the amount of volatile 14 C trapped in NaOH, and most of the radioactivity was considered to be 14 CO₂. At least six 14 C metabolites were present in the extracts of the abscised leaves treated with K^{14} CN. The extractable components in abscised leaves of cabbage over a 2 day period are shown in Table 3.

Table 3. Extractable components in abscised leaves of cabbage over a 2 day period following treatment with K¹⁴CN. (Mikami *et al.*, 1983; Report No. FM-30-0009).

		% of the applied ¹⁴ C						
	2 h	4 h	8 h	48 h				
Extracts:								
β-Cyanoalanine	0.6	0.9	0.9	0.6				
Asparagine	1.8	2.4	2.8	1.1				
Aspartic acid	0.7	1.0	1.1	1.3				
γ-Glutamyl-β-cyanoalanine	3.8	5.4	5.1	2.4				
Others	0.7	1.2	1.1	1.9				
Extracts Total	7.6	10.9	11.0	7.3				
Unextractable ¹⁴ C Total	2.9	3.7	4.5	7.7				
Treated Leaves Total	10.5	14.6	15.5	15.0				
Aqueous Solution	86.9	79.6	83.1	63.2				
Overall Total	97.4	94.2	98.6	78.2				

This study demonstrates that $H^{14}CN$ liberated on ester hydrolysis of fenpropathrin and its derivatives would be rapidly incorporated into β -cyanoalanine, asparagine, aspartic acid and γ -glutamyl- β -cyanoalanine, with ultimate formation of $^{14}CO_2$ and unextractable ^{14}C residues.

RESIDUE ANALYSIS

Analytical methods

The Meeting received information on a method of analysis developed and used in the supervised trials on black tea conducted in India (Lavakumar, S., et al., 2003; Report No. 11861 and Lavakumar, S., et al., 2004; Report No.14246). The method uses the same principle as that of the methods developed by the manufacturer and reviewed by the 1999 JMPR. The method involves extraction of fenpropathrin from black tea with an acetonitrile-water mixture (65:35). The extracts were filtered under suction and the filtrate was concentrated to approximately 150 mL. This extract was then diluted with 225 mL of 5 percent aqueous sodium chloride solution and extracted with hexane-ether mixture (8:2). The combined extracts were filtered through sodium sulphate and evaporated to near dryness before being dissolved in 5 mL of hexane. Clean-up was performed and the eluate evaporated and dissolved in acetone. Fenpropathrin was quantified by gas chromatography using an electron capture detector (ECD).

Recovery tests were conducted at a range of 0.05–2.0 mg/kg. Only the summaries of results were provided as shown in Table 4. The procedural recovery ranged between 88 and 96%. The limit of quantification (LOQ) was 0.05 mg/kg.

Table 4. Procedural recovery of fenpropathrin from fortified black tea (Lavakumar, S., et al., 2004; Report No.14246)

Fortification levels	Gree	en tea	Mad	lade tea	
(mg/kg)	Recovery	RSD	Recovery	RSD	
	%	%	%	%	
	88		88		
	88		86		
0.05	92	2.2	88	1.6	
	90		88		
	92		90		
	90		94		
	88		88		
0.5	90	1.6	92	2.7	
	90		92		
	92		94		
	88		89		
1.0	91	1.7	92	2.3	
	89		93		
	93		96		
2.0	93	0.6	93	2.3	
	92		92		
Mean	90		91		

The Meeting also received information from the Government of India on the method described in the Journal of AOAC (1999) and used in some of supervised trials conducted in India. The method uses the same principle as that of the methods developed by the manufacturer and reviewed by the 1999 JMPR. Twenty grams of black tea sample was extracted with 150 mL of acetonitrile:water (2:1, v/v) for two hours. The contents were filtered and 200 mL of 4% NaCl and 60 mL of hexane were added to the filtrate. After partitioning, the hexane layer was passed through an anhydrous sodium sulfate layer. The extract was evaporated to dryness and the residue was dissolved in 10 mL of hexane. About 30 mL of hexane-saturated acetonitrile was added and the acetonitrile layer was drained onto anhydrous sodium sulfate. The acetonitrile extract was then evaporated to dryness at 60°C. The concentrated residue was dissolved in 5 mL of hexane and cleaned up using 10 g of 5% deactivated Florisil and 150 mL of 6% diethyl ether in hexane as the eluting solvent. Prior to elution the column was washed with 50 mL of hexane. The eluate collected was concentrated at about 60°C to dryness and diluted with 10 mL of hexane and quantified by gas chromatography using ECD detector.

The LOQ was claimed to be 0.05 mg/kg. Method validation was attempted by analysis of fortified black tea samples at 0.283 mg/kg, much higher than the claimed LOQ. No recovery test was reported at 0.05 mg/kg. Only the summary of results was provided as shown in Table 5.

Table 5. Procedural recovery of fenpropathrin from fortified tea leaves.

Fortification levels	Tea leaves (green)				
(mg/kg)	Recovery	RSD			
	%	%			
	89				
	90				
0.283	83				
	95				
	103				
Mean	92	8.1			

USE PATTERN

Fenpropathrin is registered for the control of mites in tea. The label from India was provided and the Indian GAP is summarized in Table 6.

Table 6. Registered use of fenpropathrin on tea.

		F	Formulation		Application				PHI
Crop	Country	or		Method	Rate	Spray conc.	Water	No.	days
		G			kg ai/ha	kg ai/hLl	L/ha		
Tea	India	F	300 EC	Foliar	0.05 - 0.06	0.01 - 0.015	400 – 500	1	7

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information and results of supervised trials conducted in India. The application rate and method, information on varieties, plot size and sampling were provided. The residues in control plots were all below the LOQ and therefore not recorded in the following tables. Residue data are not adjusted for recovery. When residues were not detected they are shown as below the LOQ. Residues, application rates and spray concentrations have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure.

Data according to GAP are double-underlined. Data from trials not in accordance with GAP but used for the estimation of maximum residue level are single-underlined. No procedural recovery information was available for the analysis of samples from supervised trials.

Black Tea

All supervised trials on black tea were conducted in India. Matured tea leaves were collected from each plot and processed¹. In the trials conducted in 2004, and reported in Report No. 14246, leaves were processed by machine drying.

¹ The good manufacturing practice of black tea in India is as follows (Submission from the Government of India):

Withering: Harvested tea shoots were spread at a thickness of 2.5 cm and allowed to wither under ambient conditions for a period of 16-20 hours.

CTC. The withered leaves were passed into a rolling machine and rolled for 30 minutes. The rolled leaves were taken out and passed thrice through the CTC (Crush, Tear & Curl) machine, to give three cuts.

Oxidation (Fermentation): The rolled CTC tea, was spread over fermenting trays at a thickness of 1.3 - 1.8 cm for a period of one hour. Humidity was maintained at 90-95%.

Drying: The fermented 'dhool' (ground, fermented green tea shoot) was put on drying chamber. Hot air was blown over the tea with an inlet temperature of about 95-115° C. After 30 minutes of drying, dried tea was obtained with 2-3% moisture.

The results of these trials are summarized in Table 7.

Table 7. Fenpropathrin residues in black tea from supervised trials in India.

season (variety) GAP 300 EC Valparai, India January 2002 Season I (UPASI-9) Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I (UPASI-9) Valparai, India January 2002 Season I (UPASI-9)	0.05- 0.06 0.06 0.06	Water L/ha 400 -500 400 400 400	No. 1 1	days 7 0 1 3 5 7 10 14 0 1 3 5 7 10 14 0 1 3 5 7 10 10 10 10 10 10 10 10 10 10 10 10 10	mg/kg 2.74 1.75 1.17 0.61 0.17 < 0.05 < 0.05 2.69 1.69 1.10 0.61 0.18 < 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861)
GAP Valparai, India January 2002 Season I (UPASI-9) Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I Valparai, India January 2002 Season I	0.06	400	1	0 1 3 5 7 10 14 0 1 3 5 7 10 14 0 1 3 5 7	$\begin{array}{c} 1.75 \\ 1.17 \\ 0.61 \\ \underline{0.17} \\ < 0.05 \\ < 0.05 \\ \hline 2.69 \\ 1.69 \\ 1.10 \\ 0.61 \\ \underline{0.18} \\ < 0.05 \\ < 0.05 \\ \hline 2.22 \\ 1.45 \\ 0.91 \\ 0.49 \\ \underline{0.14} \\ \end{array}$	2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
January 2002 Season I (UPASI-9) Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I Seas	0.06	400	1	1 3 5 7 10 14 0 1 3 5 7 10 14 0 1 3 5 7	$\begin{array}{c} 1.75 \\ 1.17 \\ 0.61 \\ \underline{0.17} \\ < 0.05 \\ < 0.05 \\ \hline 2.69 \\ 1.69 \\ 1.10 \\ 0.61 \\ \underline{0.18} \\ < 0.05 \\ < 0.05 \\ \hline 2.22 \\ 1.45 \\ 0.91 \\ 0.49 \\ \underline{0.14} \\ \end{array}$	2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
Season I (UPASI-9) Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		3 5 7 10 14 0 1 3 5 7 10 14 0 1 3 5 7	$\begin{array}{c} 1.17 \\ 0.61 \\ \underline{0.17} \\ < 0.05 \\ < 0.05 \\ \hline 2.69 \\ 1.69 \\ 1.10 \\ 0.61 \\ \underline{0.18} \\ < 0.05 \\ < 0.05 \\ \hline 2.22 \\ 1.45 \\ 0.91 \\ 0.49 \\ \underline{0.14} \\ \end{array}$	(Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		5 7 10 14 0 1 3 5 7 10 14 0 1 3 5 7	$\begin{array}{c} 0.61 \\ \underline{0.17} \\ < 0.05 \\ < 0.05 \\ \hline \\ 2.69 \\ 1.69 \\ 1.10 \\ 0.61 \\ \underline{0.18} \\ < 0.05 \\ < 0.05 \\ \hline \\ 2.22 \\ 1.45 \\ 0.91 \\ 0.49 \\ \underline{0.14} \\ \end{array}$	also in Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
Valparai, India September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I Season I	0.06	400		7 10 14 0 1 3 5 7 10 14 0 1 3 5 7	0.17 < 0.05 < 0.05 2.69 1.69 1.10 0.61 0.18 < 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	Submission of the Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		10 14 0 1 3 5 7 10 14 0 1 3 5 7	< 0.05 < 0.05 2.69 1.69 1.10 0.61 0.18 < 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	Government of India Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		14 0 1 3 5 7 10 14 0 1 3 5 7	<0.05 2.69 1.69 1.10 0.61 0.18 <0.05 <0.05 2.22 1.45 0.91 0.49 0.14	Lavakumar, S., et al., 2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		0 1 3 5 7 10 14 0 1 3 5 7	2.69 1.69 1.10 0.61 0.18 < 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
September 2002 Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I	0.06	400		1 3 5 7 10 14 0 1 3 5 7	1.69 1.10 0.61 <u>0.18</u> < 0.05 < 0.05 2.22 1.45 0.91 0.49 <u>0.14</u>	2003 (Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
Season II (UPASI-9) Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I			1	3 5 7 10 14 0 1 3 5 7	1.10 0.61 <u>0.18</u> < 0.05 < 0.05 2.22 1.45 0.91 0.49 <u>0.14</u>	(Report No. 11861) also in Submission of the Government of India Lavakumar, S., et al., 2003
Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I			1	5 7 10 14 0 1 3 5 7	0.61 <u>0.18</u> < 0.05 < 0.05 2.22 1.45 0.91 0.49 <u>0.14</u>	also in Submission of the Government of India Lavakumar, S., et al., 2003
Valparai, India May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I Season I			1	7 10 14 0 1 3 5 7	0.18 < 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	Submission of the Government of India Lavakumar, S., et al., 2003
May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I 300 EC			1	10 14 0 1 3 5 7	< 0.05 < 0.05 2.22 1.45 0.91 0.49 0.14	Government of India Lavakumar, S., et al., 2003
May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I 300 EC			1	14 0 1 3 5 7	< 0.05 2.22 1.45 0.91 0.49 0.14	Lavakumar, S., <i>et al.</i> , 2003
May 2003 Season III (UPASI-9) Valparai, India January 2002 Season I 300 EC			1	1 3 5 7	2.22 1.45 0.91 0.49 <u>0.14</u>	2003
Season III (UPASI-9) Valparai, India January 2002 Season I Season I	0.12	400		3 5 7	0.91 0.49 <u>0.14</u>	
(UPASI-9) Valparai, India January 2002 Season I 300 EC	0.12	400		5 7	0.49 <u>0.14</u>	(Report No. 11861)
Valparai, India January 2002 Season I	0.12	400		7	<u>0.14</u>	
January 2002 Season I	0.12	400				
January 2002 Season I	0.12	400		10		1
January 2002 Season I	0.12	400		1.4	< 0.05	
January 2002 Season I	0.12	400	1	14 0	< 0.05 5.47	Lavakumar, S., et al.,
Season I			1	1	3.47	2003
	1			3	2.24	(Report No. 11861)
				5	1.04	(Report 10: 11001)
` ´ l				7	0.37	
				10	< 0.05	
				14	< 0.05	
Valparai, India 300 EC	0.12	400	1	0	5.24	Lavakumar, S., et al.,
September 2002				1	3.02	2003
Season II				3	2.22	(Report No. 11861)
(UPASI-9)				5 7	1.08 0.36	
				10	< 0.05	
				14	< 0.05	
Valparai, India May 300 EC	0.12	400	1	0	4.40	Lavakumar, S., et al.,
2003	***		_	1	2.57	2003
Season III				3	1.89	(Report No. 11861)
(UPASI-9)				5	0.86	
				7	0.30	
				10	< 0.05	
7/1 : 1 E 200 FG	0.06	400		14	< 0.05	T 1 0 1
Valparai, India 300 EC	0.06	400	1	0	0.85	Lavakumar, S., et al.,
January 2004 Fourth Season				3	0.50 0.17	2004 (Report No. 14246)
(UPASI-9)				5	< 0.17	also in
(017101-7)				7	< 0.05 < 0.05	Submission of the
				10	< 0.05	Government of India
				14	< 0.05	
Valparai, India 300 EC	0.12	400	1	0	1.62	Lavakumar, S., et al.,
January 2004				1	0.93	2004
Fourth Season				3	0.30	(Report No. 14246)
(UPASI-9)				5	< 0.05	
				7	< 0.05	
				10 14	< 0.05 < 0.05	

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country, month/year,		Applica	tion		PHI	Residues ¹	Reference
season	Form	kg ai/ha	Water	No.	days	mg/kg	
(variety)			L/ha				
Gudalur, India	300 EC	0.06	450	1	0	2.22	Submission of the
June 2004					7	<u>0.14</u> < 0.05	Government of India
(Mixed clones)					10	< 0.05	
					14	< 0.05	
Tocklai, India	300 EC	0.03	400	1	0	12.0	Submission of the
November 2005					7	<u>1.38</u>	Government of India
(Mixed clones)					10	0.12	

¹Average of three replications.

Green Tea

All supervised trials on green tea were conducted in India. Samples leaves were air dried after harvest. The results of these trials are summarized in Table 8. No procedural recovery information was available for the analysis of samples from supervised trials.

Table 8. Fenpropathrin residues in green tea from supervised trials in India

country, month/year,		Applicat	ion		PHI	Residues ¹	Reference
season	Form	kg ai/ha	Water	No.	days	mg/kg	
(variety)			Ll/ha				
GAP	300 EC	0.05-0.06	400-500	1	7		
Valparai, India	300 EC	0.06	400	1	0	1.96	Lavakumar, S., et al.,
January 2004					1	1.32	2004
Fourth Season					3	0.83	(Report No. 14246)
(UPASI-9)					5	0.45	
					7	<u>0.13</u>	
					10	< 0.05	
					14	< 0.05	
Valparai, India	300 EC	0.12	400	1	0	4.20	Lavakumar, S., et al.,
January 2004					1	2.43	2004
Fourth Season					3	1.55	(Report No. 14246)
(UPASI-9)					5	0.90	
					7	0.29	
					10	< 0.05	
					14	< 0.05	

¹Average of three replicates.

FATE OF RESIDUES IN STORAGE AND IN PROCESSING

Processing tea into tea decoctions

Processing studies were conducted in India to determine the residues in tea decoctions from leaf tea samples treated with fenpropathrin (Lavakumar, S., et al., 2004; Report No. 14246).

The trials consisted of application of an EC formulation containing 300 g ai/L of fenpropathrin at three treatment regimes involving different use rates: (i) a single application at a rate of 0.06 kg ai/ha; (ii) a single application at a rate of 0.12 kg ai/ha; (iii) untreated. Samples were collected at 0, 1, 3, 5, 7, 10 and 14 days after application. Fifty grams of leaf tea sample was collected and boiled in 100 mL of water for 5 minutes in a 500 mL conical flask. This was then filtered and concentrated to 10mL. Partitioning and clean-up were then carried out as described in the method of analysis for black tea. Residues of fenpropathrin in the tea decoctions were determined by gas chromatography with electron capture detection (ECD). No information was available on procedural recoveries for the analysis of samples

A transfer factor was used to indicate the amount of fenpropathrin transferred from tea leaves to water (decoction) during brewing.

The transfer factor was calculated by dividing the total residue in mg in the decoction (concentrated to 10 mL) by the total residue in mg in tea leaves (50 g) assuming that the specific gravity of the decoction is the same as that of water. A precise processing factor could not be estimated because the residue levels in decoction before concentration were too low to quantify.

The results are summarized in Tables 9 and 10.

Table 9. Fenpropathrin residues in black tea decoctions from supervised trials in India (Lavakumar, S., *et al.*, 2004; Report No. 14246).

Country,	PHI	Residues	1 (mg/kg)	Transfer factor	Reference
month/year,	(days)	Black tea	Tea decoction		
season			(10 ml)		
(variety)					
Valparai, India	0	0.85	0.13	0.03	Lavakumar, S., <i>et al.</i> , 2004
January 2004	1	0.50	< 0.05	< 0.02	(Report No. 14246)
Fourth Season	3	0.17	< 0.05	< 0.06	
(UPASI-9)	5	< 0.05	< 0.05		
	7	< 0.05	< 0.05		
	10	< 0.05	< 0.05		
	14	< 0.05	< 0.05		
Valparai, India	0	1.62	0.18	0.02	Lavakumar, S., et al., 2004
January 2004	1	0.93	< 0.05	< 0.01	(Report No. 14246)
Fourth Season	3	0.30	< 0.05	< 0.03	
(UPASI-9)	5	< 0.05	< 0.05		
	7	< 0.05	< 0.05		
	10	< 0.05	< 0.05		
	14	< 0.05	< 0.05		

¹Average of three replicates.

Table 10. Fenpropathrin residues in green tea decoctions from supervised trials in India (Lavakumar, S., *et al.*, 2004; Report No. 14246).

Country,	PHI	Residues	¹ (mg/kg)	Transfer factor	Reference
month/year, season (variety)	(days)	Green tea	Tea decoction (10 ml)		
Valparai, India	0	1.96	0.11	0.01	Lavakumar, S., et al., 2004
January 2004	1	1.32	< 0.05	< 0.008	(Report No. 14246)
Fourth Season	3	0.83	< 0.05	< 0.01	
(UPASI-9)	5	0.45	< 0.05	< 0.02	
	7	0.13	< 0.05	< 0.08	
	10	< 0.05	< 0.05		
	14	< 0.05	< 0.05		
Valparai, India	0	4.20	0.25	0.01	Lavakumar, S., et al., 2004
January 2004	1	2.43	< 0.05	< 0.004	(Report No. 14246)
Fourth Season	3	1.55	< 0.05	< 0.006	
(UPASI-9)	5	0.90	< 0.05	< 0.01	
	7	0.29	< 0.05	< 0.03	
	10	< 0.05	< 0.05		
	14	< 0.05	< 0.05		

¹Average of three replicates.

APPRAISAL

Fenpropathrin, an insecticide/acaricide, was first evaluated by the JMPR in 1993 as a new compound. The JMPR allocated an ADI of 0-0.03 mg/kg and recommended 14 MRLs, later adopted by the Codex Alimentarius Commission as Codex MRLs. The residue definition is fenpropathrin (the residue is fat soluble).

At the 38th Session of the CCPR in 2006, the Delegation of India requested the elaboration of an MRL for tea. Fenpropathrin was added to the agenda of the current Meeting for evaluation pending

availability of trial data on tea. The Meeting received the current label from India, results of supervised trials, a processing and plant metabolism study and methods of analysis.

Metabolism

Plant metabolism

The Meeting received studies conducted to determine metabolism of fenpropathrin in leaves.

The metabolism of radio-labelled fenpropathrin was investigated in cabbages grown and treated in a greenhouse. After foliar application of ¹⁴C -fenpropathrin to cabbages the radioactive carbon on the surface of treated leaves decreased as ¹⁴C in the leaves increased. Most of the recovered radiocarbon was in the treated leaves and less than 1.2% of the applied radioactive carbon was found in the untreated shoots. This indicates that fenpropathrin and its metabolites only slightly translocate from the site of application to other parts of the plant. The predominant radioactive component in the surface washes was the parent compound, fenpropathrin. The major radioactive components in leaves were fenpropathrin and the conjugates of metabolites with a –CH2OH group.

The fate of HCN and 2,2,3,3-tetramethylcyclopropanecarboxylic acid (TMPA) in abscised leaves of apple, cabbage, kidney bean, mandarin orange, tomato and vine was investigated. TMPA was readily converted in plants to more polar products. In orange, cabbages and bean plants, the malonyl glucoside was mainly formed. In tomato, the gentiobioside was predominant. Further work was carried out using $K^{14}CN$. There was a gradual increase in the amount of volatile ^{14}C trapped in NaOH solution, most of the radioactive carbon was considered to be $^{14}CO_2$. The study demonstrates that $H^{14}CN$ liberated on ester hydrolysis of fenpropathrin and its derivatives would be rapidly incorporated into β -cyanoalanine, asparagine, aspartic acid and γ -glutamyl- β -cyanoalanine, with ultimate formation of $^{14}CO_2$ and unextractable ^{14}C residues.

The Meeting confirmed that the residue definition of fenpropathrin is appropriate for leafy vegetables as well as for tea.

Methods of residue analysis

The Meeting received descriptions and validation data for methods of analysis used in the supervised trials on tea conducted in India.

Both methods use the same principle as that of the methods developed by the manufacturer and reviewed by the 1999 JMPR and involve extraction of fenpropathrin, partitioning, clean-up and analysis using GC-ECD. For one method, recovery test were conducted at a range of 0.05–2 mg/kg and procedural recoveries in this range were 88–96%. The limit of quantification was 0.05 mg/kg. For the second method, a recovery test was conducted at 0.283 mg/kg resulting in procedural recovery around 90%. No details for the procedural recovery tests were reported for either method.

Results of supervised trials on crops

The Meeting received information and results from a total of 12 supervised trials conducted in India on tea. The current product label from India was provided. No information was available for procedural recoveries in the analysis of samples from supervised trials.

Tea

Fenpropathrin (300 g ai/kg EC) is registered in India for use on tea at 0.05–0.06 kg ai/ha with a PHI of 7 days.

In ten trials, collected tea leaves were processed into black tea. In six trials this was achieved through withering, crush/tear/curl process, oxidation and drying while in another two trials by machine drying. In trials with conditions matching the registered use, residues of fenpropathrin were in rank order: < 0.05, 0.14, 0.14, 0.17 and 0.18 mg/kg. In one trial conducted with double rates, the residues in

the black tea from the sample taken 7 days after treatment were < 0.05 mg/kg. In another trial conducted with half rates, the residues in black tea from the sample taken 7 days after treatment were 1.38 mg/kg. No information on the possible cause of the high residue concentration was available. Although the used rate was half of the Indian GAP rate, the Meeting decided to include this value for estimating the maximum residue level.

In two additional trials, collected tea leaves were air-dried to prepare green tea. In trials where conditions matching the registered use pattern, residues of fenpropathrin were 0.13 mg/kg.

Since growing conditions and application rate/method for black tea and green tea are equivalent with the only difference being in processing methods, the Meeting estimated a maximum residue level for tea, green, black on the basis of combined residue results: < 0.05 (2), 0.13, 0.14, 0.14, 0.17, 0.18 and 1.38 mg/kg.

The Meeting estimated a maximum residue level, STMR and HR at 2 mg/kg, 0.14 mg/kg and 1.38 mg/kg respectively.

Fate of residues during processing

The Meeting received information on the fate of fenpropathrin during the brewing of tea.

Black tea (50 g) from field trials at the maximum rate or green tea (50 g) from trials at the maximum rate or double rates was brewed by boiling in 100 mL of water in a flask. Tea samples and concentrated decoctions were analyzed. However, no information was available on procedural recoveries for the analysis of samples.

A transfer factor was used to indicate the amount of fenpropathrin transferred from tea leaves to water (decoction) during brewing. The transfer factor was tentatively calculated by dividing the total residue (mg) in the decoction (concentrated to 10 mL) by the total residue (mg) in tea leaves (50 g) assuming that the specific gravity of the decoction is the same as that of water. No estimation of the processing factor was possible as the residue levels in the decoction before concentration were too low to quantify. The results indicate that only a small amount of fenpropathrin was transferred into the decoction as predicted from the highly fat-soluble nature of the compound. Table 3 shows the calculated transfer factor.

Table 11. Transfer factor from tea to decoction.

Process	Transfer factor	Best estimate
Black tea - decoction	0.03, < 0.02, < 0.06	0.03
	0.02, < 0.01, < 0.03	
Green tea - decoction	0.01, < 0.008, < 0.01, < 0.02, < 0.08	0.01
	0.01, < 0.004, < 0.006, < 0.01, < 0.03	

Where the residues in black or green tea were below the LOQ, the transfer factor was not calculated.

RECOMMENDATIONS

On the basis of the data from supervised trials on tea, the Meeting concluded that the residue concentration below is suitable for establishing an MRL and for assessing dietary intakes.

Definition of the residue: fenpropathrin

The residue is fat soluble.

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Table 12. Summary of recommendations.

Commodity		Recommended MRL mg/kg		STMR/ STMR-P	HR/HR-P mg/kg
CCN	Name	New	Previous	mg/kg	
DT 1114	Tea, Green, Black	2	-	0.14	1.38

DIETARY RISK ASSESSMENT

Long-term intake

The long-term dietary intakes were estimated for the 13 cluster diets using maximum residue levels for fenpropathrin recommended by the 1999 Meeting and an STMR for tea estimated by the current. The maximum ADI is 0.03 mg/kg and the calculated intakes were 3–80% of the maximum ADI. The Meeting concluded that the long-term intake of residues of fenpropathrin resulting from the uses considered by the Meeting was unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTIs) of fenpropathrin by general population and by children were calculated for tea, green, black, for which an HR was estimated by the current Meeting. As it is not known if it is necessary to establish an ARfD, no the short-term intake assessment could be determined.

REFERENCES

Author, Date, Title, Institute, Report Reference, Document No.

Mikami, N. et al. 1983. Metabolism of Fenpropathrin in Plants, Laboratory of Biochemistry and Toxicology, Takarazuka Research Center, Sumitomo Chemical Co., Ltd., Report No. FM-30-0009, Unpublished Report No. 11861 FM-30-0009

Lavakumar, S., *et al.* 2003. Studies on the three season residues of Fenpropathrin 30% w/w EC in black tea and soil, International Institute of Biotechnology and Toxicology (IIBAT), Tamil Nadu, India, Study No. 04-2974-2002, Report No. 11861, Unpublished Report No. 1424604-2974-2002

Lavakumar, S., *et al.* 2004. Studies on the residues of Fenpropathrin 30% w/w EC in tea and soil (fourth season), International Institute of Biotechnology and Toxicology (IIBAT), Tamil Nadu, India,, Study No. 04-4190-2004, Report No. 14246, Unpublished04-4190-2004

Anonymous 2005. (March) Submission of the Government of India: Data information required for CCPR/JMPR evaluations for fixation of MRL of fenpropathrin in tea (Group 24 – TEAS, Codex Classification Group 066: Teas)